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DEVICE FOR ABSORBING OR COLLECTING A LIQUID

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FIELD OF THE INVENTION

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This invention relates to a device for absorbing liquid, especially liquid spills. Applications include control and absorption of household or industrial spills (i.e. a "sponge"); control and absorption of oil spills at sea; control and absorption of blood during medical emergencies and operations; etc.

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A sponge is an absorbent article, usually having an open porous structure. The open porous structure may be made from natural or synthetic material. In general, the more open and porous the structure is, the greater is its capacity for absorbing and holding liquid. However, the more open and porous the structure is, the lower capillary forces are exerted and consequently the liquid and the liquid readily drains out of the sponge; whereas the less porous the structure is, the higher the capillary forces are exerted but the liquid is absorbed comparatively slowly.

US-A-5 834 385, issued on November 10th 1998, discloses a nonwoven hydrophobic membrane which encases an absorbent core, the whole article being of use to clear up oil spills. Pore sizes of the membrane are not disclosed.

5 US-A-5 678 564, issued on October 21st, 1997, discloses a system provided with a membrane which has and is capable of maintaining a vacuum on one side so that when liquid contacts the opposite side of the membrane the liquid passes through the membrane and is removed by a maintained vacuum to a receptacle device for disposal.

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The object of the present invention is to provide a device for absorbing or collecting liquid, such as a sponge, which comprises a liquid reservoir and a porous membrane. Liquid passing into the liquid reservoir to be absorbed must pass through the porous membrane which drives the rate of absorbency. More
15 rapid rates of absorbency are possible than can be achieved using prior art methods and devices.

In one aspect of the present invention the liquid reservoir has an open porous structure, and in an alternative embodiment the liquid reservoir comprises
20 a void space.

SUMMARY OF THE INVENTION

25 The object of the invention is achieved by providing a membrane which is hermetically sealed to or around the reservoir so that fluid passing through the inlet must pass across the membrane, and wherein the membrane has an average pore size of from 1 to 100 micrometers.

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DETAILED DESCRIPTION OF THE INVENTION

The devices of the present invention work on the principle of a "closed distribution system". By "closed distribution system" it is meant herein that a membrane is saturated with a liquid and that air is prevented from entering the system even under vacuum, provided the vacuum pressure does not exceed the bubble point pressure of the membrane. Liquid can then be drawn across the membrane into the closed distribution system, for example by capillary effects. Once liquid is inside the closed distribution system it is rapidly absorbed.

The term "fluid" as used herein means liquid or gas

The term "hermetically sealed" as used herein means that a gas (especially air) can neither pass from the outside environment to the inside of the reservoir; nor from the inside of the reservoir to the outside environment, when the membrane is saturated with liquid as long as the pressure differential across the membrane does not exceed the bubble point pressure. In particular the membrane to reservoir seal, or the membrane to membrane seal prevents the leakage of gas across the sealed region.

The membrane has an average pore size of no more than 100 micrometers, preferably no more than 50 micrometers, more preferably no more than 10 micrometers, and most preferably of no more than 5 micrometers. It is also preferred that the membrane has a pore size of at least 1 micrometer, preferably at least 3 micrometers. It is further preferred that the pore size distribution is such that 95% of the pores have a size of no more than 100 micrometers, preferably no more than 50 micrometers, more preferably no more than 10 micrometers, and most preferably of no more than 5 micrometers.

The membrane has an average thickness of less than 1mm, preferably less than 100 micrometers, more preferably less than 30 micrometers, and even more preferably the membrane has an average thickness of no more than 10 micrometers, and most preferably of no more than 5 micrometers.

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The term "oleophilic" as used herein refers to materials having a receding contact angle for the oily liquid to be transported of less than 90 degrees, preferably less than 70 degrees, more preferably less than 50 degrees, even more preferably less than 20 degrees, and most preferably less than 10 degrees.

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The term "hydrophilic" as used herein refers to materials having a receding contact angle for distilled water of less than 90 degrees, preferably less than 70 degrees, more preferably less than 50 degrees, even more preferably less than 20 degrees, and most preferably less than 10 degrees.

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For convenience the device for absorbing a liquid will be referred to hereinafter as a sponge. The term "sponge" is used generically herein and is not intended to be limiting.

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In one aspect, the present invention is concerned with a sponge which is based upon direct suction rather than on capillarity. Therein, the liquid is transported through a region into which substantially no air (or other gas) should enter (at all, or at least not in a significant amount). The driving force for liquid flowing through such a sponge can be created by a liquid source (e.g. a spill) in liquid communication with the sponge, either externally or internally. The direct suction is maintained by ensuring that substantially no air or gas enters the sponge. This means that the membrane should be substantially air impermeable up to a certain pressure, namely the bubble point pressure. Thus, a sponge must have a certain liquid permeability. A higher liquid permeability provides less flow resistance, and thus is preferred from this point of view.

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However, for conventional porous liquid transport materials, those materials that function based on capillary transport mechanisms (also referred to herein as "bulk materials"), liquid transport is generally controlled by the interaction of pore size and permeability, such that open, highly permeable structures will generally be comprised of relatively large pores. These large pores provide highly permeable structures, however these structures have very limited wicking heights for a given set of respective surface energies, i.e., a given combination of type of material and liquids. Pore size can also affect liquid retention under normal use conditions.

In contrast to such conventional capillary governed mechanisms, in the present invention, these conventional limitations have been overcome, as it has been surprisingly found that materials exhibiting a relatively lower permeability (e.g. "membrane") can be combined with material exhibiting a relatively higher permeability (e.g. "bulk materials"), and the combination provides significant synergistic effects.

In particular, it has been found that when a highly liquid permeable material having large pores filled with liquid is surrounded by a material having essentially no air permeability up to a certain pressure, the bubble point pressure, but having also relatively low liquid permeability, the composite sponge will have a high liquid permeability and a high bubble point pressure at the same time, thus allowing very fast liquid transport.

Bulk material

A key requirement for the bulk region is to have a low average flow resistance, such as expressed by having a permeability k of at least 10^{-11} m^2 ,

preferably more than 10^{-8} m²., more preferably more than 10^{-7} m², and most preferably more than 10^{-5} m². One important means to achieve such high permeabilities for the bulk materials can be achieved by utilizing material providing relatively high porosity. Such a porosity, which is commonly defined as
5 the ratio of the volume of the materials that makes up the porous materials to the total volume of the porous materials, and as determined via density measurements commonly known, should be at least 50%, preferably at least 80%, more preferably at least 90%, or even exceeding 98%, or 99%.

10 In the extreme of the bulk material essentially consisting of a single pore, or void space, the porosity approaches or even reaches 100%. In this case the liquid reservoir is defined by a wall region, and the volume of the liquid reservoir is variable. Preferably the volume is varied either by flexibly deforming the wall region, or by the action of a piston.

15 The bulk material can have pores, which are larger than about 200 μ m, 500 μ m, 1 mm or even 9 mm in diameter or more. Such pores may be smaller prior to the fluid transport, such that the bulk material may have a smaller volume, and expand just prior or at the liquid contact. Preferably, if such pores are
20 compressed or collapsed, they should be able to expand by a volumetric expansion factor of at least 5, preferably more than 10. Such an expansion can be achieved by materials having an elastic modulus of more than the external pressure which, however, must be smaller than the bubble point pressure. High porosities can be achieved by a number of materials, well known in the art as
25 such. For example fibrous members can readily achieve such porosity values. Non-limiting examples for such fibrous materials that can be comprised in the bulk region are high-loft non-wovens, e.g., made from polyolefin or polyester fibers as used in the hygienic article field, or car industry, or for upholstery or HVAC industry. Other examples comprise fiber webs made from cellulosic fibers.

Such porosities can further be achieved by porous, open celled foam structures, such as, without intending any limitation, for example polyurethane reticulated foams, cellulose sponges, or open cell foams as made by the High Internal Phase Emulsion Polymerization process (HIPE foams), all well known from a variety of industrial applications such as filtering technology, upholstery, hygiene and so on. Such porosities can be achieved by wall regions which circumscribe voids defining the bulk material, such as exemplified by pipes. Alternatively, several smaller pipes can be bundled. Such porosities can further be achieved by "space holders", such as springs, spacer, particulate material, corrugated structures and the like. The bulk material pore sizes or permeabilities can be homogeneous throughout the bulk material, or can be inhomogeneous.

It is not necessary, that the high porosity of the bulk material is maintained throughout all stages between manufacture and use of the sponge, but the voids within the bulk material can be created shortly before or during its intended use. For example, bellow like structures held together by suitable means can be activated by a user, and during its expansion, the liquid penetrates through a port region into the expanding bulk material, thereby filling the sponge completely or at least sufficiently to not hinder the liquid flow. Alternatively, open celled foam materials, such as described in (US-A-5 563 179 or US-A-5 387 207) have the tendency to collapse upon removal of water, and the ability to re-expand upon re-wetting. Thus, such foams can be transported from the manufacturing site to the user in a relatively dry, and hence thin (or low-volume), and only upon contact with the source liquid increase their volume so as to satisfy the void permeability requirements.

The bulk material can have various forms or shapes. The bulk material can be cylindrical, ellipsoidal, sheet like, stripe like, or can have any irregular shape. The bulk material can have constant cross-sectional area, with constant or

varying cross-sectional shape, like rectangular, triangular, circular, elliptical, or irregular.

The absolute size of the bulk material should be selected to suitably match the geometric requirements of the intended use. Generally, it will be desirable to have the minimum dimension for the intended use. The benefit of the designs according to the present invention is to allow much smaller cross-sectional areas than conventional materials. The dimensions of the bulk material are determined by the permeability of said bulk material, which can be very high, due to possible large pores, as the bulk material does not have to be designed under the contradicting requirements of high flux (i.e. large pores) and high vertical liquid transport (i.e. small pores). Such large permeabilities allow much smaller cross-sections, and hence very different designs.

The bulk material can be essentially non-deformable, i.e. maintains its shape, form, volume under the normal conditions of the intended use. However, in many uses, it will be desirable, that the bulk material allows the complete sponge to remain soft and pliable. The bulk material can change its shape, such as under deforming forces or pressures during use, or under the influence of the fluid itself. The deformability or absence thereof can be achieved by selection of one or more materials as the bulk material (such as a fibrous member).

The confining separations of the bulk material may further comprise materials which significantly change their properties upon wetting, or which even may dissolve upon wetting. Thus, the bulk material may comprise an open cell foam material having a relatively small pore at least partially being made of soluble material, such as polyvinylalcohol or the like. The small porosity can draw in liquid at the initial phase of liquid transport, and then rapidly dissolve so as to then leave large voids filled with liquid. Alternatively, such materials may fill larger pores, completely or partially. For example, the bulk material can comprise

soluble materials, such as poly(vinyl) alcohol or poly(vinyl) acetate. Such materials can fill the voids, or support a collapsed state of the voids before the sponge is contacted with liquid. Upon contact with liquid, such as oil or water, these materials may dissolve and thereby create empty or expanded voids.

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Membrane

The term "membrane" as used herein is generally defined as a material or region that is permeable for liquid, gas or a suspension of particles in a liquid or gas. The membrane may for example comprise a microporous region to provide liquid permeability through the capillaries. Microporous hydrophobic membranes will typically allow gas to permeate, while water-based liquids will not be transported through the membrane if the driving pressure is below a threshold pressure commonly referred to as "breakthrough" or "bridging" pressure. In contrast, hydrophilic microporous membranes will transport water based liquids. Once wetted, however, gases (e.g. air) will essentially not pass through the membrane if the driving pressure is below a threshold pressure commonly referred to as "bubble point pressure". Hydrophilic monolithic films will typically allow water vapour to permeate, while gas will not be transported rapidly through the membrane. Similarly membranes can also be used for non-water based liquids such as oils. For example most hydrophobic materials will be in fact oleophilic. A hydrophobic microporous membrane will therefore be permeable for oil but not for water and can be used to absorb and transport oil, or to separate oil and water.

Membranes are often produced as thin sheets, and they can be used alone or in combination with a support layer (e.g. a nonwoven) or in a support element (e.g. a spiral holder). Other forms of membranes include but are not limited to

polymeric thin layers directly coated onto another material, bags corrugated sheets.

Further known membranes are "activatable" or "switchable" membranes that can change their properties after activation or in response to a stimulus. This change in properties might be permanent or reversible depending on the specific use. For example, a hydrophobic microporous layer may be coated with a thin dissolvable layer e.g. made from poly(vinyl)alcohol. Such a double layer system will be impermeable to gas. However, once wetted and the poly(vinyl)alcohol film has been dissolved, the system will be permeable for gas but still impermeable for liquid. Conversely, if a hydrophilic membrane is coated by such a soluble layer, it might become activated upon liquid contact to allow liquid to pass through, but not air.

Another useful membrane parameter is the permeability to thickness ratio, which in the context of the present invention is referred to as "membrane conductivity". This reflects the fact that, for a given driving force, the amount of liquid penetrating through a material such as a membrane is on one side proportional to the permeability of the material, i.e. the higher the permeability, the more liquid will penetrate, and on the other side inversely proportional to the thickness of the material. Hence, a material having a lower permeability compared to the same material having a decrease in thickness, shows that thickness can compensate for this permeability deficiency (when regarding high rates as being desirable). Typical k/d for sponges according to the present invention is from about 1×10^{-9} to about 500×10^{-9} m, preferably from about 100×10^{-9} to about 500×10^{-9} m. Preferably the k/d is at least 1×10^{-7} and more preferably at least 1×10^{-5} m.

For a porous membrane to be functional once wetted (permeable for liquid, not-permeable for air), at least a continuous layer of pores of the membrane

always need to be filled with liquid and not with gas or air. Therefore evaporation of the liquid from the membrane pores must be minimized, either by a decrease of the vapour pressure in the liquid or by an increase in the vapour pressure of the air, or by sealing the sponge into a non-permeable wrap, such as a film of polyethylene.

As noted hereinabove the device of the present invention is particularly useful for cleaning domestic or industrial spills from, for example, hard surfaces. The present invention may also be applied in the medical field, for example for absorbing blood or other bodily fluids.

It may be desirable to separate, as completely as possible, oil from water. In a most preferred embodiment of the present invention the device effectively separates oil from water, for example, by selection of a suitable oleophilic and hydrophobic membrane.

Test method: Bubble Point Pressure (membrane)

The following procedure applies when it is desired to assess the bubble point pressure of a membrane.

First, the membrane material is connected with a plastic funnel (available from Fischer Scientific in Nidderau, Germany, catalog number 625 617 20) and a length of tube. The funnel and the tube are connected in an air tight way. Sealing can be made with Parafilm M (available from Fischer Scientific in Nidderau, Germany, catalog number 617 800 02). A circular piece of membrane material, slightly larger than the open area of the funnel, is sealed in an air tight way with the funnel. Sealing is made with suitable adhesive, e.g. Pattex from Henkel KGA, Germany). The lower end of the tube is left open i.e. not covered by a membrane

material. The tube should be of sufficient length, i.e. up to 10m length may be required.

In case the test material is very thin, or fragile, it can be appropriate to support it by a very open support structure (as e.g. a layer of open pore non-woven material) before connecting it with the funnel and the tube.

In case the test specimen is not of sufficient size, the funnel may be replaced by a smaller one (e.g. Catalog # 625 616 02 from Fisher Scientific in Nidderau). If the test specimen is too large size, a representative piece can be cut out so as to fit the funnel.

The testing liquid can be the transported liquid (i.e. oil or grease), but for ease of comparison, the testing liquid should be a solution 0.03% TRITON X-100, such as available from MERCK KGaA, Darmstadt, Germany, under the catalog number 1.08603, in distilled or deionized water, thus resulting in a surface tension of 33 mN/m. Whilst keeping the lower (open) end of the funnel within the liquid in the reservoir, the part of the funnel with the membrane is taken out of the liquid. If appropriate, but not necessarily, the funnel with the membrane material should remain horizontally aligned.

Whilst slowly continuing to raise the membrane above the reservoir, the height is monitored, and it is carefully observed through the funnel or through the membrane itself (optionally aided by appropriate lighting) if air bubbles start to enter through the material into the inner of the funnel. At this point, the height above the reservoir is registered to be the bubble point height.

From this height H the Bubble point pressure BPP is calculated as:
 $BPP = \rho \cdot g \cdot H$ with the liquid density ρ , gravity constant g ($g \approx 9.81 \text{ m/s}^2$).

In particular for bubble point pressures exceeding about 50 kPa, an alternative determination can be used, such as commonly used for assessing bubble point pressures for membranes used in filtration systems. Therein, the membrane is separating two liquid filled chambers, when one is set under an increased gas pressure (such as an air pressure), and the point is registered when the first air bubbles "break through".

Determination of Pore Size

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Optical determination of pore size is especially used for thin layers of porous system by using standard image analysis procedures know to the skilled person.

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The principle of the method consists of the following steps: 1) A thin layer of the sample material is prepared by either slicing a thick sample into thinner sheets or if the sample itself is thin by using it directly. The term "thin" refers to achieving a sample caliper low enough to allow a clear cross-section image under the microscope. Typical sample calipers are below 200 μ m. 2) A microscopic image is obtained via a video microscope using the appropriate magnification. Best results are obtained if about 10 to 100 pores are visible on said image. The image is then digitized by a standard image analysis package such as OPTIMAS by BioScan Corp. which runs under Windows 95 on a typical IBM compatible PC. Frame grabber of sufficient pixel resolution (preferred at least 1024 x 1024 pixels) should be used to obtain good results. 3) The image is converted to a binary image using an appropriate threshold level such that the pores visible on the image are marked as object areas in white and the rest remains black. Automatic threshold setting procedures such as available under OPTIMAS can be used. 4) The areas of the individual pores (objects) are determined. OPTIMAS offers fully automatic determination of the areas. 5) The

equivalent radius for each pore is determined by a circle that would have the same area as the pore. If A is the area of the pore, then the equivalent radius is given by $r=(A/\pi)^{1/2}$. The average pore size can then be determined from the pore size distribution using standard statistical rules. For materials that have a not
5 very uniform pore size it is recommended to use at least 3 samples for the determination.

Optionally commercially available test equipment such as a Capillary Flow Porometer with a pressure range of 0-1380 kPa (0-200psi), such as supplied by
10 Porous Materials, Inc, Ithaca, New York, US model no. CFP-1200AEXI, such as further described in respective user manual of 2/97, can also be used to determine bubble point pressure, pore size and pore size distribution.

15 Determination of caliper

The caliper of the wet sample is measured (if necessary after a stabilization time of 30 seconds) under the desired compression pressure for which the experiment will be run by using a conventional caliper gauge (such as supplied
20 by AMES, Waltham, MASS, US) having a pressure foot diameter of 1 1/8 " (about 2.86 cm), exerting a pressure of 0.2 psi (about 1.4 kPa) on the sample, unless otherwise desired.

25 Determination of permeability and conductivity

Permeability and conductivity are conveniently measured on commercially available test equipment.

For example, equipment is commercially available as a Permeameter such as supplied by Porous Materials, Inc, Ithaca, New York, US under the designation PMI Liquid Permeameter. This equipment includes two Stainless Steel Frits as porous screens, also specified in said brochure. The equipment
5 consists of the sample cell, inlet reservoir, outlet reservoir, and waste reservoir and respective filling and emptying valves and connections, an electronic scale, and a computerized monitoring and valve control unit. A detailed explanation of a suitable test method using this equipment is also given in the applicants co-
pending application PCT/US98/13497, filed on 29th June 1998 (attorney docket
10 no. CM1841FQ).

Example

15 A sponge comprises a polyurethane bulk material completely surrounded by a polyamide membrane. The membrane is sealed to itself at both ends of the sponge, as well as along the length of the sponge so that all fluid passing into or out of the sponge must pass through the membrane. The membrane has an
average pore size of 20 micrometers, an open area of 14%, a caliper of 55
20 micrometers and is manufactured by Sefar Inc., of Ruschlikon, Switzerland, number 03-20/14. The bulk material which is 100 mm long, 90 mm wide and 5 mm deep, it has 10 pores per inch, and is manufactured by Kureta of
Stadtallendorf, Germany (K-S ppi 10).